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INTERIM REPORT
on
ELECTRICAL CONDUCTION AND THERMIONIC
EMISSION IN SEMI-CONDUCTORS

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1. Conductivity of thorium oxide crystals in various atmospheres.

Investigation of the electrical conductivity of crystalline thorium in different gases at atmospheric pressure has been made. Optically clear specimens of fused thorium were cut into rectangular slabs of approximately 5 mm length. Two faces of these crystals were platinum coated by evaporation in vacuo. The specimens were pressed between platinum plates by springs and heated in a furnace. Temperature readings were taken with a Pt-Pt/10 Rh thermocouple spotwelded on one of the platinum plates. The experimental arrangement is shown in Figure 1. To make sure that no resistance due to possible thorium-platinum interfaces obscured the measurements, a large specimen, cylindrical in shape, was made. This was fitted with potential probes. It was seen that conductivity values determined by volt-ampere measurements across the ends were identical with those obtained by measuring the probe potentials.

In general, the values of conductivity obtained when the crystal was heated in a hydrogen atmosphere followed the usual temperature dependence for a semi-conductor; $\sigma = A \exp(-eV/kT)$. The value of eV obtained from the data of Fig. 2 is 1.25. For two other specimens, values of 1.15 and 1.28 were obtained.

The conductivity in oxygen was noticeably higher, as shown in Figure 2. Unlike the values obtained in hydrogen, the values obtained in oxygen at low temperature do not appear to be highly

reproducible. If the crystal is in oxygen, and the temperature is lowered from 1100° to (for example) 700° C, the conductivity at the latter temperature will be seen to decrease with time. The data obtained at the higher temperatures in oxygen are reproducible and give a value of $eV = 0.74$.

The measurements have all been obtained with the use of the circuit of Figure 1. Current was allowed to flow through the specimen only long enough for the voltage across the capacitor to come to equilibrium. This equilibrium voltage, being proportional to the current and the value of the resistor R_1 , gives a measure of current which can be read on the electrometer meter after the measurement is actually made. This is essentially a pulsed method of measurement, and the total charge passed through the crystal for each observation is very small. These precautions are necessary since, if current is drawn continuously the conductivity of the specimen may be drastically altered.

2. Effect of passage of current on conductivity and colour.

Figure 3 shows the type of change which occurs when a crystal, heated to 675° C in oxygen, passes current continuously. The value of conductivity at zero time is an equilibrium value obtained by pulse measurement. The current passed by the crystal with a fixed voltage applied is seen to increase with time of current drawing, to a new equilibrium value. When the applied voltage is removed, the conductivity decays to its original value, the points along the decay curve (not shown) being obtained by pulse measurements. Curve II of this figure shows an even larger ratio

of change at 580° .

When current is passed continuously through a thorium crystal heated in hydrogen, very little conductivity change occurs. If the atmosphere is changed from hydrogen to helium, a conductivity increase of two orders of magnitude occurs at 680° when current is passed continuously. This is shown in the latter part of Figure 4.

In past reports it has been noted that the conductivity change and color change occur simultaneously when the atmosphere in which the thorium crystal is being heated is changed from oxygen to hydrogen. This type of change has now been studied more extensively and the results are shown in part in Figure 4. It is important to note the method whereby the colour was ascertained at a particular stage of the experiment. The conductivity measurements are made, of course, with the crystal at the temperature noted on the curve, and the desired gas flowing around it. If the colour is to be ascertained, the crystal on its supporting structure is drawn out to a cool section which extends outside the furnace. After about one minute, the crystal will be cool enough for its color to be noted. It is then returned to the hot area and conductivity measurements resumed. By colour, then, is meant that colour which is observed when the crystal is cooled rather rapidly in the atmosphere in which it has been heated.

Referring to Figure 4, it is seen that the conductivity change in helium was not accompanied by complete bleaching from the original red color which was present in oxygen. This observation was not conclusive since it is obvious from the figure that the

conductivity change had not gone to completion. On admitting hydrogen, simultaneous rapid bleaching and drop of conductivity were observed. At the conclusion of this process, the atmosphere was again changed back to helium with no effect on the conductivity (observed by the pulsed method) or on the color. Now the large conductivity change due to current drawing in helium (as previously described) was produced, and this was found to be accompanied by a return to the original red coloration. The rapidity of this change is strongly dependent upon the current density.

It has been stated that if the crystal was held in hydrogen, and the conductivity measured by infrequent short pulses, no conductivity or colour changes occurred, the crystal being bleached and the conductivity low. If current was passed continuously when the thorium crystal was heated in hydrogen, a blackening of the crystal took place, appearing first at the cathode end of the crystal and spreading out toward the anode, so that finally the whole crystal was black. The blackening progressed at the rate of about 3 mm for each coulomb passed through the crystal. If the current was reversed after the crystal was blackened part way across, the first blackened area would appear to recede toward the new anode, while a new area of blackness would appear at the new cathode. Thus it is supposed that the blackening is associated with the migration of positive carriers, either metal ions or oxygen vacancies. The blackening produced could not be bleached out by heating the crystal in either vacuum or inert gas or hydrogen. It could be partly removed by heating the crystal in oxygen, but even this treatment would not restore the specimen to its

original optical clarity; cloudiness and irregular dark areas would still be present.

3. Solubility of hydrogen in thorium oxide crystals.

In the preceding report (May 31, 1952) experiments were described involving the bleaching and conductivity change of a heated thoria crystal when the atmosphere around it was changed from oxygen to hydrogen. In order to further understand the role of hydrogen in causing the bleaching and lowered conductivity, it was felt necessary to determine whether the hydrogen could enter the thoria crystal, in sufficient quantity to account for the changes observed. The red coloration is assumed to be due to the presence of excess oxygen acting as f-centers, also producing p-type semi-conductor behaviour. The most sensitive measurement available has failed to show any weight change associated with the reddening of a crystal in oxygen, or the bleaching of a red crystal either in hydrogen or vacuum. The results of this work indicate an upper limit of the amount of excess oxygen in the neighborhood of 2×10^{17} atoms/cc of thoria. Measurement of the gas evolved when a crystal was bleached in vacuum indicated that this figure is of the correct order.

A number of oxygen-reddened crystals totalling 12 grams in weight were bleached at a temperature of 1000° C in hydrogen at one atmosphere pressure. They were then placed in a vacuum system with gas collection and analysis system attached. (This system is described in Reports of Contract NObser-52592 dated November 15, 1951 and June 15, 1952). The crystals were heated

to 1000°C in this system, and the gas evolved measured and analysed. Successive runs of this experiment gave analyses of 80%, 120% and 95% as the hydrogen content of the evolved gas. The scatter, and the value above 100% are due to the inherent inaccuracy of the system when small quantities of gas are analysed. Thus we interpret the results as showing that substantially 100 of the gas evolved was hydrogen.

In the first run of this experiment, 2 mm^3 of gas (80% hydrogen analysis) were collected. In a subsequent run, made more carefully, it was seen that the quantity q evolved up to time t roughly followed the form $q = Q(1 - e^{-kt})$. The shape of the curve was not accurately fitted (perhaps due to variations of temperature of $\pm 30^{\circ}$). However, the asymptote seemed clearly enough indicated to enable one to determine the total quantity Q with reasonable accuracy. The total amount of gas dissolved in the thorium oxide crystals then turned out to be about $5\text{ mm}^3(\text{STP})$, which analysed about 100% hydrogen. The latter value was obtained twice. Taking the value of 5 mm^3 as most accurate, the amount of hydrogen dissolved in 1 cc of thorium oxide under the conditions initially given is about 2.5×10^{17} atoms. Thus it is found that the number of hydrogen atoms which enter the crystal when it is bleached are of the same order as the number of excess oxygen atoms which were estimated to be present. The remarkably good agreement is undoubtedly fortuitous, as none of the measurements involved pretend to this degree of accuracy.

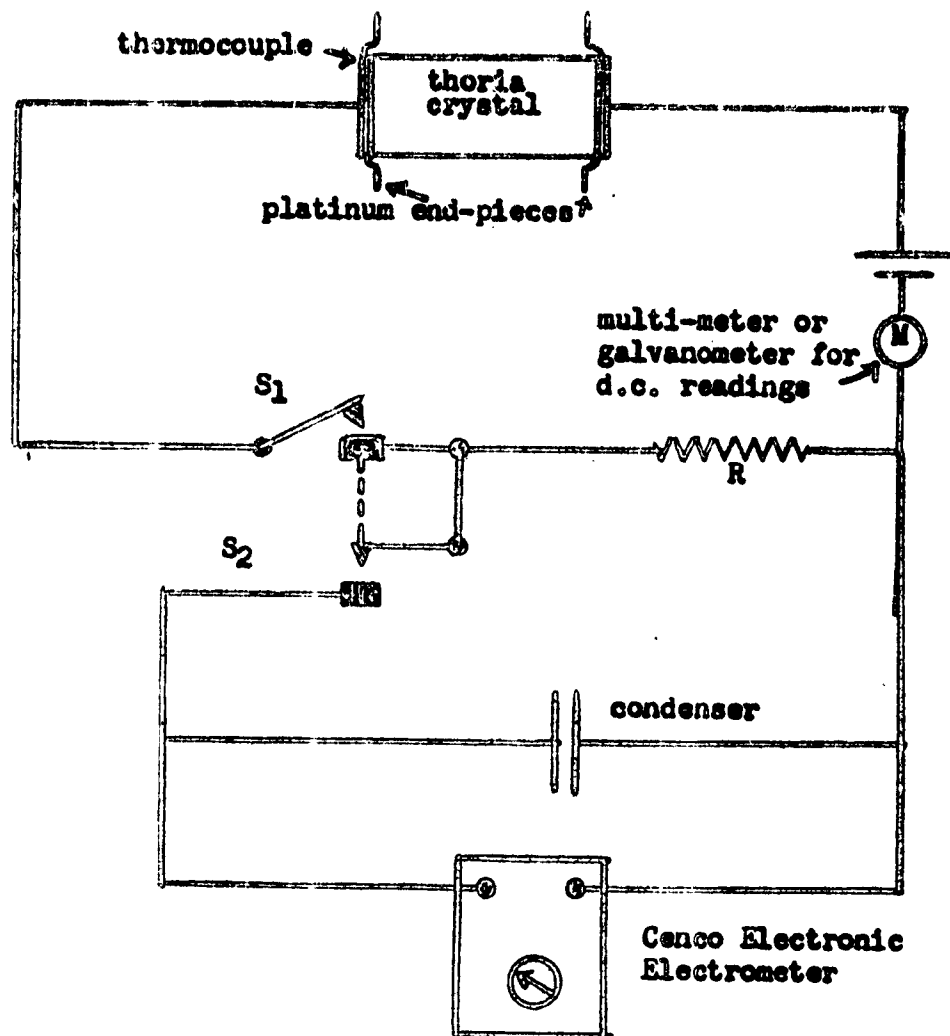


FIGURE 1. Schematic Representation of Experimental Arrangement.

The thermocouple is connected to a Leeds & Northrup Type K Potentiometer.

The mechanical linkage between S_1 and S_2 is such that both may be closed by pressing S_1 ; and after both are closed, if the pressure is released, S_2 must open first. When both are closed, current starts to flow through the crystal and the condenser starts to charge. After the condenser-resistor combination has reached equilibrium, the switches are opened, and since S_2 opens first, the voltage on the condenser represents the current which was flowing. The time constant of the isolated condenser-electrometer circuit is so long that the reading may be made for many seconds after S_2 is opened. The arrangement has been worked out in practice so that the whole cycle above described is performed by tapping S_1 momentarily, and a current reading may be obtained while passing only a small total charge through the crystal.

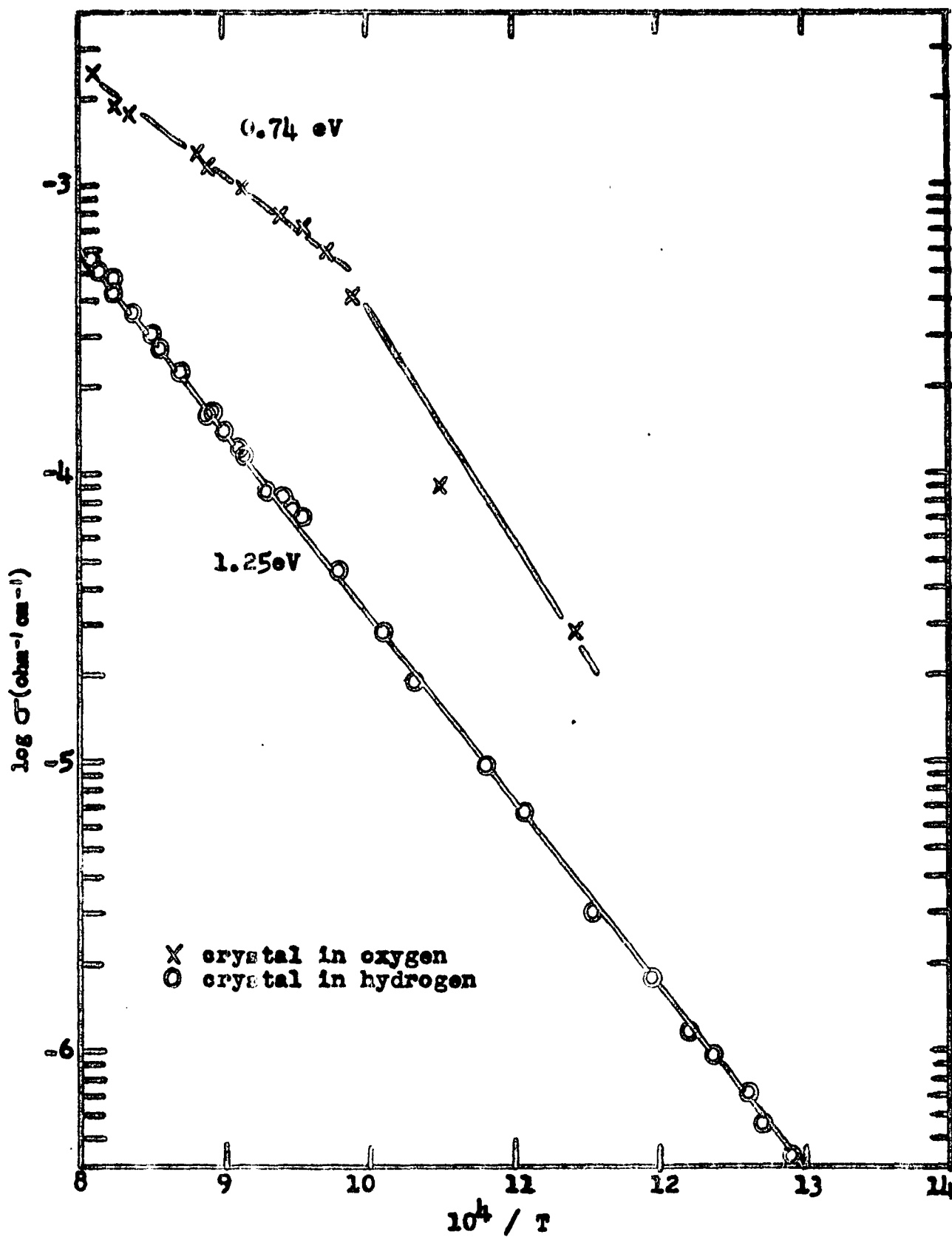
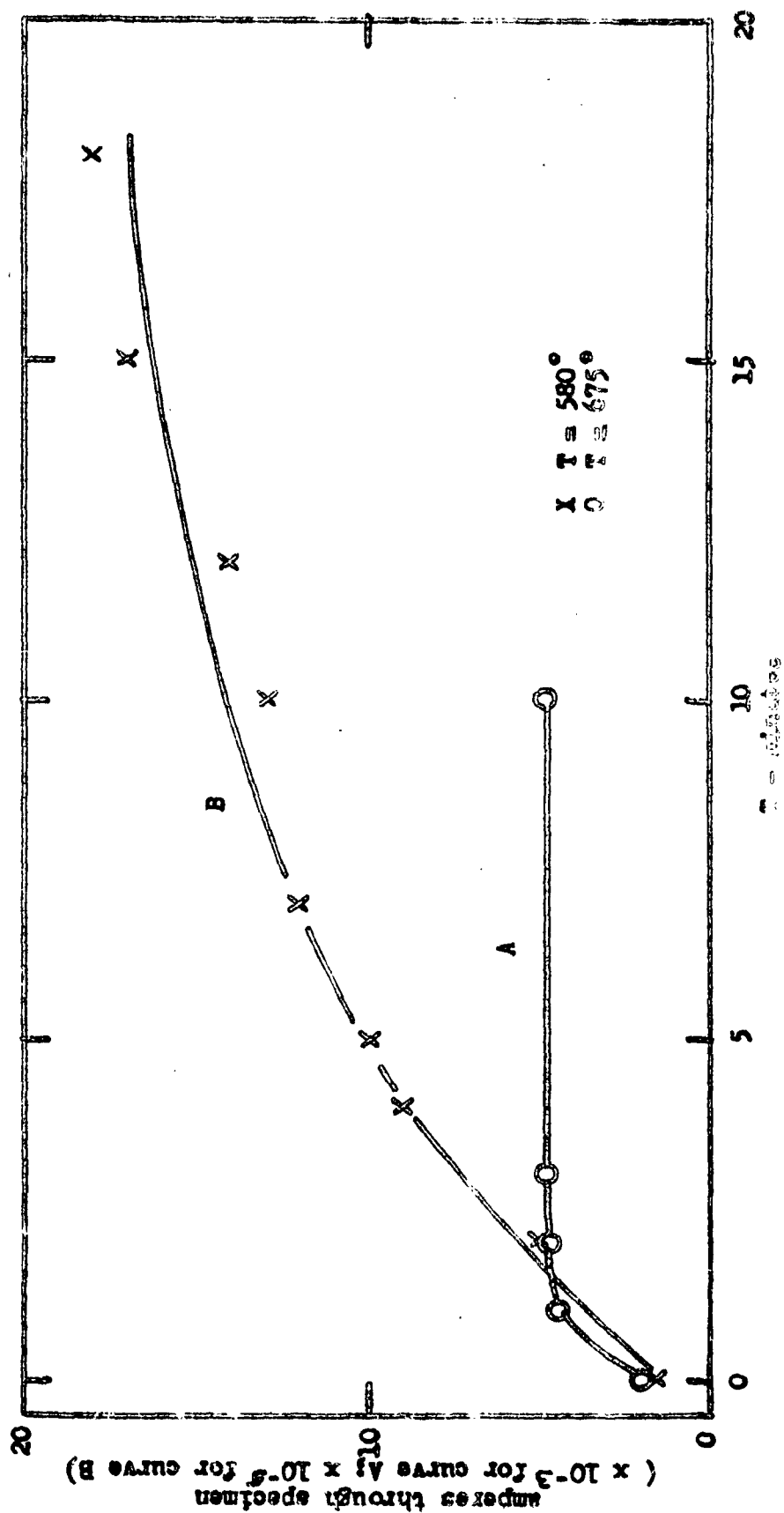


FIGURE 2 - Conductivity of thoria in oxygen and hydrogen.

FIGURE 3. Conductivity of thoria in oxygen at two temperatures. Current was passed continuously during each run. The ordinate is given in terms of current; since this current was passed at constant voltage, the ordinate scale may be considered to be conductivity in arbitrary units.



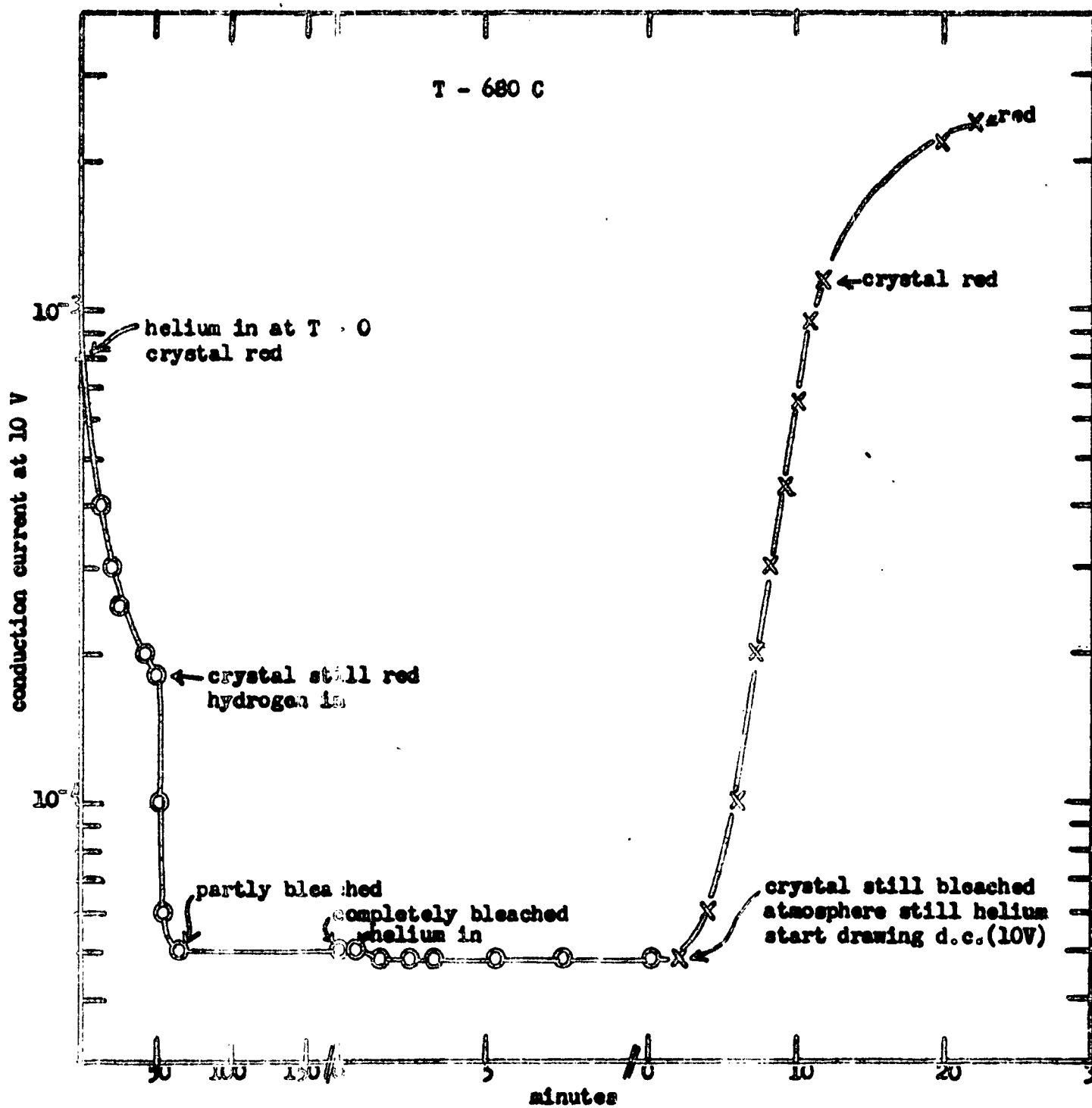


FIGURE 4 - Changes of color and conductivity